

PATENT ABSTRACTS OF JAPAN

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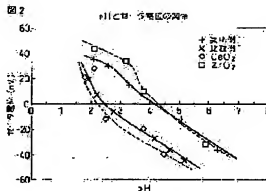
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(54) CERIUM-ZIRCONIUM COMPOUND METALLIC OXIDE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a cerium-zirconium compound oxide having improved durability at high temperature and stable OSC (oxygen storage capacity) performance.

SOLUTION: The cerium-zirconium compound metallic oxide has at least 85% of the total mole number of Ce and Zr with respect to the whole metal mole number in the compound metallic oxide, 1/9 to 9/1 molar ratio of Ce/Zr and over 3.5 isoelectric point of the compound metallic oxide. Preferably the compound metallic oxide has 3/7 to 7/3 molar ratio of Ce/Zr and 3.8 to 5.0 isoelectric point and contains rare earth metals (excluding Ce) by <15 mol% with respect to the total metal mole number in the material. The cerium-zirconium compound metallic oxide contains CeO₂ as nuclei and ZrO₂ present around the nuclei.



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CLAIMS

[Claim(s)]

[Claim 1]Are a cerium zirconium composite metal oxide and on the basis of the total number of metal mols in said composite metal oxide, A cerium zirconium composite metal oxide which the number of sum total mols of Ce and Zr is at least 85%, and mole ratios of Ce/Zr are 1 / 9 - 9/1, and is characterized by an isoelectric point of said composite metal oxide exceeding 3.5.

[Claim 2]The cerium zirconium composite metal oxide according to claim 1 in which mole ratios of said Ce/Zr are 3 / 7 - 7/3, and said isoelectric points are 3.8-5.0.

[Claim 3]The cerium zirconium composite metal oxide according to claim 1 or 2 which contains a rare earth metal (except for Ce) less than [15 mol %] on the basis of the total number of metal mols in said composite metal material.

[Claim 4]Are a cerium zirconium composite metal oxide and on the basis of the total number of metal mols in said composite metal oxide, A cerium zirconium composite metal oxide, wherein the number of sum total mols of Ce and Zr is at least 85%, it uses CeO_2 as a core and ZrO_2 exists in the surroundings of the core.

[Claim 5]The cerium zirconium composite metal oxide according to claim 4 in which a core of said CeO_2 has a diameter which is 5-20 nm.

[Claim 6]A catalyst for exhaust gas purification, wherein the precious metals are supported by cerium zirconium composite metal oxide given in any 1 paragraph of claims 1-5.

[Claim 7]ceria -- sol and a zirconium compound solution, or zirconia -- a synthesizing method of the cerium zirconium composite metal oxide according to claim 1 or 4 characterized by drying and calcinating after mixing sol and preparing suspension.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]About a cerium zirconium composite metal oxide, this invention is divided and relates to a cerium zirconium composite metal oxide suitable for being used for the catalyst for exhaust gas purification of an internal-combustion engine as a co-catalyst.

[0002]

[Description of the Prior Art]Although nitrogen oxides (NO_x), carbon monoxide (CO), hydrocarbon (HC), etc. are contained in the exhaust gas discharged from internal-combustion engines, such as car motor, While these toxic substances oxidize CO and HC, the three way component catalyst etc. which return NO_x to O_2 can purify them. Generally this three way component catalyst supports the catalyst component of the precious metals, such as platinum (Pt), palladium (Pd), and rhodium (Rh), to the carrier of oxides, such as gamma-alumina, and is constituted.

[0003]In order for oxidation of CO and HC and reduction of NO_x to advance efficiently in such a three way component catalyst, it is required to control the air-fuel ratio of an internal-combustion engine appropriately, and to be in the narrow range with specific exhaust gas composition. However, it may happen to change exhaust gas composition to some extent, and to separate from the specific narrow range by the time lag of a control system, etc., actually.

[0004]Here, the cerium zirconium multiple oxide can produce valence change of trivalent and tetravalence. [atom / which is contained / Ce] And by the oxidizing atmosphere included comparatively mostly, O_2 . Ce atom can produce valence change from trivalent in tetravalence, oxygen can be absorbed, and the oxygen occlusion ability (OSC) that Ce atom produces valence change from tetravalence in trivalent, and emits oxygen can be demonstrated in the reducing atmosphere containing comparatively many COs and HC. Therefore, if a cerium zirconium multiple oxide is included in the catalyst for exhaust gas purification, change of exhaust gas composition [/ near the catalyst component] is eased,

and the above-mentioned exhaust gas purification can be advanced more efficiently.

[0005]In addition, since remarkable generation of heat arises in connection with the oxygen uptake of a cerium zirconium multiple oxide, this generation of heat can be used for warming up of the catalyst at the time of engine start, and the start period of catalytic activity can be brought forward. For this reason, the cerium zirconium multiple oxide is used as a co-catalyst of the catalyst for exhaust gas purification. There are JP,10-194742,A, JP,6-279027,A, etc. as advanced technology of this cerium zirconium multiple oxide.

[0006]

[Problem(s) to be Solved by the Invention]However, generally, when such a cerium zirconium multiple oxide is put to not less than about 1000 °C elevated temperature for a long period of time, it causes the fall of OSC ability and has the problem that endurance is not enough. Therefore, the endurance under an elevated temperature is improved and an object of this invention is to provide the cerium zirconium multiple oxide which has the stable OSC ability.

[0007]

[Means for Solving the Problem]The above-mentioned purpose is a cerium zirconium composite metal oxide, and on the basis of the total number of metal mols in said composite metal material, it is attained by cerium zirconium composite metal oxide which the number of sum total mols of Ce and Zr is at least 85%, and mole ratios of Ce/Zr are 1 / 9 - 9/1, and is characterized by an isoelectric point of said composite metal oxide exceeding 3.5.

[0008]That is, this invention is a cerium zirconium composite metal oxide which has a specific presentation, and is a cerium zirconium composite metal oxide having an isoelectric point which divides and exceeds 3.5.

[0009]This "isoelectric point" is weighted solidity measured based on electrophoresis of particles in a slurry, in a method of specifying by this invention, an isoelectric point of CeO_2 is 2.4 and an isoelectric point of ZrO_2 is 4.0. That is, while a cerium zirconium composite metal oxide of this invention includes both sides of CeO_2 and ZrO_2 , it has an isoelectric point near ZrO_2 .

[0010]As this isoelectric point, a cerium zirconium composite metal oxide of this invention has a value whose presentation of CeO_2 and ZrO_2 is notably higher than a cerium zirconium composite metal oxide of equivalent conventional technology. Durable performance of a catalyst for exhaust gas purification which supports Pt to this cerium zirconium composite metal oxide is improved more notably than that of conventional technology.

[0011]From these things, a cerium zirconium composite metal oxide of this invention, in the outside, particles which constitute it mainly present [ZrO_2 and the inside] a state like drawing 1 which mainly consists of CeO_2 , and it is thought that especially such a state is

stabilized when a little elements chosen as ZrO_2 from a rare earth metal live together.

Namely, this invention is a cerium zirconium composite metal oxide in another aspect of affairs, It is a cerium zirconium composite metal oxide, wherein the number of sum total mols of Ce and Zr is at least 85%, it uses CeO_2 as a core and ZrO_2 exists in the surroundings of the core on the basis of the total number of metal mols in said composite metal oxide.

[0012]When ZrO_2 and CeO_2 present such an existence gestalt, Heat-resistant high ZrO_2 holds a gestalt of particles of a cerium zirconium composite metal oxide, and it by it. Inside CeO_2 and/or CeO_2 - ZrO_2 of a border area of the inside and the outside are presumed to stabilize temporally and to be able to demonstrate OSC ability. Drawing 1 is an explanatory view strictly like a model, and does not limit this invention.

[0013]

[Embodiment of the Invention]This invention is a cerium zirconium composite metal oxide, and on the basis of the total number of metal mols in said composite metal oxide, It is characterized by the isoelectric point of said composite metal oxide exceeding 3.5, and more preferably, the number of sum total mols of Ce and Zr is at least 85%, and the mole ratios of Ce/Zr are $1/9 - 9/1$, and said isoelectric points are [the mole ratios of said Ce/Zr are $3/7 - 7/3$, and] 3.8-5.0. In this invention, an "isoelectric point" is defined as the value measured by JIS R1638 with the stopwatch method which is one of the electrophoresis microscopic methods of a statement.

[0014]A "cerium zirconium composite metal oxide" is an oxide which can contain Ce and Zr at least and can contain another "metal." Can choose this another "metal" from s-block metal, d-block metal, p-block metal, and f-block metal broadly, and specifically, Sodium (Na), potassium (K), magnesium (Mg), calcium (Ca), Barium (Ba), strontium (Sr), a lanthanum (La), yttrium (Y), Cerium (Ce), PURASEOJIUMU (Pr), neodymium (Nd), samarium (Sm), A europium (Eu), gadolinium (Gd), titanium (Ti), tin (Sn), A zirconium (Zr), manganese (Mn), iron (Fe), cobalt (Co), They can be nickel (nickel), chromium (Cr), niobium (Nb), copper (Cu), and vanadium (V), molybdenum (Mo), tungsten (W), zinc (Zn), aluminum (aluminum), silicon (Si), tantalum (Ta), etc.

[0015]Preferably, the another above-mentioned "metal" is at least one sort of rare earth metals, such as La, Y, Ce, Pr, Nd, Sm, Eu, and Gd, and is contained in the quantity below 15 mol % on the basis of the total number of metal mols in a cerium zirconium composite metal oxide. When "metal" is these rare earth metals, it is thought that especially nuclear surrounding ZrO_2 is stabilized.

[0016]This cerium zirconium composite metal oxide, desirable -- as the source of cerium -- ceria -- being manufactured using sol -- ceria -- sol. and a zirconium compound solution or zirconia -- after mixing the metal compound solution or sol of sol and desirable another "metal" at a predetermined rate and preparing suspension, it can obtain by drying and

calcinating.

[0017]here -- "ceria -- sol -- " -- "zirconia -- sol -- " -- etc. -- with "sol." Are colloid of the oxide of a fluid especially distributed in water, or a hydrate, mean the substance which calcinates and generates metallic oxides, such as Seria and zirconia, and specifically, The substance produced by hydrolyzing alkoxides, such as cerium or a zirconium, acetylacetone, acetate, a nitrate, etc. in a solution is illustrated. Solution, such as oxyzirconium nitrate $\text{ZrO}(\text{NO}_3)_2$ and $2\text{H}_2\text{O}$, and zirconium chloride ZrCl_4 , is illustrated by the "zirconium compound solution."

[0018]The conditions heated in 600-900 °C atmospheric air for several hours, for example are suitable for calcination. Thus, after presenting a grinding process with the obtained cerium zirconium composite metal oxide as occasion demands, the precious metals, such as platinum, palladium, and rhodium, can be supported and the catalyst for exhaust gas purification can be prepared. This catalyst for exhaust gas purification can demonstrate the stable high exhaust gas cleaning capacity, without OSC ability deteriorating intentionally, even if put to the temperature of about 1000 °C. Hereafter, an example explains this invention more concretely.

[0019]

[Example]the ceria of a 1193.33 g example -- sol (as CeO_2 -- 15 mass %.) The solution in which 100 g of ion exchange water was made to dissolve a 41.16-g oxyzirconium nitrate and 6.48 g of nitric acid yttrium was added and stirred to the Taki Chemical make and knee DORARU U-15, and uniform suspension was created.

After presenting heating of 120 °C x 24 hours with this suspension and evaporating water, calcination of 700 °C x 5 hours was presented, and the cerium zirconium composite metal oxide of following this invention of presentation (mass ratio): $\text{CeO}_2/\text{ZrO}_2/\text{Y}_2\text{O}_3=58/38/4$ was obtained.

[0020]Subsequently, 300 g of ion exchange water was made to distribute 50 g of this multiple oxide, the slurry was created, 11.36g of solution (Pt concentration 4.4 mass %) of the dinitrodiamine platinum complex was added to this slurry, and it stirred for 2 hours. Subsequently, after presenting heating of 120 °C x 24 hours with this slurry and evaporating water, calcination of 500 °C x 2 hours was presented, and the catalyst for exhaust gas purification of this invention which supported Pt of 1 mass % to the cerium zirconium content multiple oxide of this invention was acquired.

[0021]the ceria of the above of a 2193.33 g example -- with the solution which made 50 g of ion exchange water dissolve 6.48 g of nitric acid yttrium in sol. zirconia -- 95g added, sol (20 mass %, the product made from the first rare element chemical industry, zirconia HA as ZrO_2) was stirred, and uniform suspension was created.

[0022]Subsequently, like Example 1, after evaporating water from this suspension, calcination of 700 °C x 5 hours was presented, and the cerium zirconium composite metal

oxide of following this invention of presentation (mass ratio): $\text{CeO}_2/\text{ZrO}_2/\text{Y}_2\text{O}_3=58/38/4$ was obtained. Subsequently, like Example 1, Pt of 1 mass % was supported to this multiple oxide using the dinitrodiammine platinum complex, and the catalyst for exhaust gas purification of this invention was acquired.

[0023]the ceria of the above of a 3193.33 g example -- with the solution which made 50 g of ion exchange water dissolve 6.48 g of nitric acid yttrium in sol. zirconia -- 154.5g added, sol. (12.5 mass %, the first rare element chemical industry, zirconia AC7 as ZrO_2) was stirred, and uniform suspension was created.

[0024]Subsequently, like Example 1, after evaporating water from this suspension, calcination of 700×5 hours was presented, and the cerium zirconium composite metal oxide of following this invention of presentation (mass ratio): $\text{CeO}_2/\text{ZrO}_2/\text{Y}_2\text{O}_3=58/38/4$ was obtained. Subsequently, like Example 1, Pt of 1 mass % was supported to this multiple oxide using the dinitrodiammine platinum complex, and the catalyst for exhaust gas purification of this invention was acquired.

[0025]the ceria of the above of a 4193.33 g example -- to sol, the oxyzirconium nitrate of 34.66 g, the 3.99-g lanthanum nitrate, and the solution in which 8.94-g nitric acid PURASEOJIUMU was dissolved were added and stirred to 300 g of ion exchange water, and uniform suspension was created.

[0026]Subsequently, like Example 1, after evaporating water from suspension, calcination of 700×5 hours is presented, The following presentation (mass ratio): The cerium zirconium composite metal oxide of this invention of $\text{CeO}_2/\text{ZrO}_2/\text{La}_2\text{O}_3/\text{Pr}_6\text{O}_{11}=58/32/3/7$ was obtained. Subsequently, like Example 1, Pt of 1 mass % was supported to this multiple oxide using the dinitrodiammine platinum complex, and the catalyst for exhaust gas purification of this invention was acquired.

[0027]The solution in which the ion exchange water of 1500 g of comparative examples was made to dissolve a 73.165 g cerium nitrate, a 41.16-g oxyzirconium nitrate, and 6.48 g of nitric acid yttrium was created. Subsequently, the ammonia solution with a concentration of 1 mol/l. was dropped at this solution, pH was adjusted to about 9, and the sediment was produced according to coprecipitation.

[0028]Subsequently, after evaporating water like Example 1 from the solution containing this sediment, Calcination of 700×5 hours was presented, and the cerium zirconium composite metal oxide of the following comparative example of presentation (mass ratio): $\text{CeO}_2/\text{ZrO}_2/\text{Y}_2\text{O}_3=58/38/4$ was obtained. Subsequently, like Example 1, Pt of 1 mass % was supported to this multiple oxide using the dinitrodiammine platinum complex, and the catalyst for exhaust gas purification of the comparative example was acquired.

[0029]The solution in which the ion exchange water of 2500 g of comparative examples was made to dissolve a 73.17 g cerium nitrate, a 34.66 g oxyzirconium nitrate, a 3.99 g lanthanum nitrate, and 8.94-g nitric acid PURASEOJIUMU was prepared. Subsequently, a

sediment is produced from this solution according to coprecipitation like the comparative example 1, After evaporating water, calcination of 700×5 hours was presented, and the cerium zirconium composite metal oxide of the following comparative example of presentation (mass ratio): $\text{CeO}_2/\text{ZrO}_2/\text{La}_2\text{O}_3/\text{Pr}_6\text{O}_{11}=58/32/3/7$ was obtained.

Subsequently, like Example 1, Pt of 1 mass % was supported to this multiple oxide using the dinitrodiamine platinum complex, and the catalyst for exhaust gas purification of the comparative example was acquired.

[0030] The ion exchange water of 3500 g of comparative examples was made to distribute 29 g of cerium oxide powder, it ranked second, the solution made to dissolve a 41.16-g oxyzirconium nitrate and 6.48 g of nitric acid yttrium in 200 g of ion exchange water was added and stirred, and the slurry was prepared. Subsequently, the ammonia solution was dropped at this slurry like the comparative example 1, pH was adjusted to about 9, and the sediment containing a zirconium and yttrium was produced.

[0031] Subsequently, after evaporating water, calcination of 700×5 hours was presented, and the cerium zirconium composite metal oxide of the following comparative example of presentation (mass ratio): $\text{CeO}_2/\text{ZrO}_2/\text{Y}_2\text{O}_3=58/38/4$ was obtained. Subsequently, like the comparative example 1, Pt of 1 mass % was supported to this multiple oxide using the dinitrodiamine platinum complex, and the catalyst for exhaust gas purification of the comparative example was acquired.

[0032]- About each cerium zirconium composite metal oxide of the measurement-examples 1-4 and the comparative examples 1-3 of an isoelectric point, the isoelectric point was measured according to the stopwatch method which is one of the electric ***** fine mirror methods of a statement to JIS R1638. This result is summarized in Table 1 and shown. The relation of pH and F-potential which were measured in order to ask drawing 2 for an isoelectric point in the above-mentioned measuring method about the cerium zirconium composite metal oxide of Example 1 and the comparative example 1, and CeO_2 powder and ZrO_2 powder is shown.

[0033] It turns out that there is a difference clear to the isoelectric point of the cerium zirconium composite metal oxide of an example and a comparative example from these results, an example shows the isoelectric point near ZrO_2 powder, and the isoelectric point near CeO_2 powder is shown according to a comparative example. However, in Examples 1-3, the comparative examples 1 and 3 and Example 4, and the comparative example 2. Since the presentation of a cerium zirconium composite metal oxide is equivalent, these differences, It is judged as the thing originating in a CeO_2 and ZrO_2 's existence gestalt, and in an example, since ZrO_2 exists in the surroundings of it by using CeO_2 as a core as shown in drawing 1, it is thought that the isoelectric point near ZrO_2 powder is shown.

[0034]- Each catalyst for exhaust gas purification of the catalyst performance evaluation-

examples 1-4 and the comparative examples 1-3 was compressed and cracked, and catalyst performance was evaluated about 2.0g each made into a pellet about 2 mm in diameter. In order to grasp the durable improvement effect, catalyst performance was evaluated after presenting durable processing of 1000 **x 3 hours with each catalyst for exhaust gas purification.

[0035]The evaluation condition measured the purifying rate of each ingredient of C_3H_6 (HC), NO, and CO, the rich gas/lean gas of the presentation shown in Table 1 considering it as the conditions which change for every minute, and carrying out temperature up of the degree of catalyst floor temperature to 400 ** the speed for 10 **/so that the difference in OSC ability may appear in a result. Catalyst performance made the index temperature by which these ingredients are purified 50%. This result is summarized in Table 2 and shown.

[0036]

[Effect of the Invention]The endurance under an elevated temperature is improved and the cerium zirconium multiple oxide which has the stable OSC ability can be provided.

[0037]

[Table 1]

〈表1〉評価用のガス組成

	N_2 (%)	CO_2 (%)	NO (ppm)	CO (%)	C_3H_6 (ppmC)	H_2 (%)	O_2 (%)	H_2O (%)
リッチガス	バランス	10	2200	2.80	2500	0.27	0.77	10
リーンガス	バランス	10	2200	0.81	2500	0	1.7	10

[0038]

[Table 2]

〔表 2〕触媒性能と等電点の測定結果

	組 成	質量比	H ₂	NO	CO	等電点
実施例 1	Ce-Zr-Y-O	58/38/4	234	288	180	4.2
実施例 2	Ce-Zr-Y-O	58/38/4	253	288	221	3.9
実施例 3	Ce-Zr-Y-O	58/38/4	263	301	216	4.1
実施例 4	Ce-Zr-La-Pr-O	58/32/3/7	245	270	201	4.0
比較例 1	Ce-Zr-Y-O	58/38/4	280	308	242	2.5
比較例 2	Ce-Zr-La-Pr-O	58/32/3/7	269	303	253	2.2
比較例 3	Ce-Zr-Y-O	58/38/4	302	366	299	3.3

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1]It is a model figure of the cerium zirconium composite metal oxide of this invention.

[Drawing 2]It is a graph which shows the relation between pH in measurement of an isoelectric point, and F-potential.

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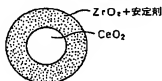
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DRAWINGS

[Drawing 1]

図 1

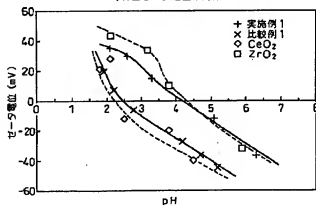
本発明のセリウム-ジルコニウム複合金属酸化物のモデル図



[Drawing 2]

図 2

pHとゼータ電位の関係



[Translation done.]

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C 0 1 G 25/00		C 0 1 G 25/00	4 D 0 4 8
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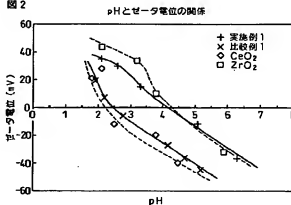
(54) 【発明の名称】 セリウム-ジルコニウム複合金属酸化物

(57) 【要約】

【課題】 高温下での耐久性が改良され、安定したOSC能を有するセリウム-ジルコニウム複合酸化物を提供する。

【解決手段】 セリウム-ジルコニウム複合金属酸化物であって、前記複合金属酸化物中の全金属モル数を基準に、CeとZrの合計モル数が少なくとも85%であり、Ce/Zrのモル比が1/9~9/1であり、かつ前記複合金属酸化物の等電点が3.5を上回ることを特徴とするセリウム-ジルコニウム複合金属酸化物である。好ましくは、前記Ce/Zrのモル比が3/7~7/3であり、前記等電点が3.8~5.0であり、希土類金属(Ceを除く)を、前記複合金属材料中の全金属モル数を基準に、15モル%未満で含む。また、本発明は、CeO₂を核とし、その核の周りにZrO₂が存在することを特徴とするセリウム-ジルコニウム複合金属酸化物である。

図2



【特許請求の範囲】

【請求項1】 セリウム-ジルコニウム複合金属酸化物であって、前記複合金属酸化物中の全金属モル数を基準に、CeとZrの合計モル数が少なくとも85%であり、Ce/Zrのモル比が1/9~9/1であり、かつ前記複合金属酸化物の等電点が3.5を上回ることを特徴とするセリウム-ジルコニウム複合金属酸化物。

【請求項2】 前記Ce/Zrのモル比が3/7~7/3であり、前記等電点が3.8~5.0である請求項1に記載のセリウム-ジルコニウム複合金属酸化物。

【請求項3】 希土類金属(Ceを除く)を、前記複合金属材料中の全金属モル数を基準に、15モル%未満で含む請求項1又は2に記載のセリウム-ジルコニウム複合金属酸化物。

【請求項4】 セリウム-ジルコニウム複合金属酸化物であって、前記複合金属酸化物中の全金属モル数を基準に、CeとZrの合計モル数が少なくとも85%であり、CeO₂を核とし、その核の周りにZrO₂が存在することを特徴とするセリウム-ジルコニウム複合金属酸化物。

【請求項5】 前記CeO₂の核が5~20nmの直径を有する請求項4に記載のセリウム-ジルコニウム複合金属酸化物。

【請求項6】 請求項1~5のいずれか1項に記載のセリウム-ジルコニウム複合金属酸化物に貴金属が担持されたことを特徴とする排気ガス浄化用触媒。

【請求項7】 セリアゾル、及びジルコニウム化合物溶液又はジルコニアゾルを混合して懸濁液を調製した後、乾燥・焼成することを特徴とする請求項1又は4に記載のセリウム-ジルコニウム複合金属酸化物の合成方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、セリウム-ジルコニウム複合金属酸化物に関し、とりわけ、内燃機関の排気ガス浄化用触媒に助触媒として使用されるのに適するセリウム-ジルコニウム複合金属酸化物に関する。

【0002】

【従来の技術】自動車用エンジン等の内燃機関から排出される排気ガスには、窒素酸化物(NO_x)、一酸化炭素(CO)、炭化水素(HC)等が含まれるが、これらの有害物質は、COとHCを酸化すると同時に、NO_xをO₂に還元する三元触媒等によって浄化することができる。かかる三元触媒は、一般に、白金(Pt)、パラジウム(Pd)、ロジウム(Rh)等の貴金属の触媒成分をγ-アルミナ等の酸化物の担体に担持して構成される。

【0003】こうした三元触媒においてCOとHCの酸化、及びNO_xの還元が効率的に進行するためには、内燃機関の空燃比が適切に制御されて、排気ガス組成が特定の狭い範囲にあることが必要である。しかし、実際には、制御系の時間遅れ等によって排気ガス組成がある程

度変動し、特定の狭い範囲から外れることが起こり得る。

【0004】ここで、セリウム-ジルコニウム複合酸化物は、含まれるCe原子が3価と4価の価数変化を生じることができる。そして、O₂を比較的多く含む酸化性雰囲気では、Ce原子が3価から4価に価数変化を生じて酸素を吸収し、COとHCを比較的多く含む還元性雰囲気では、Ce原子が4価から3価に価数変化を生じて酸素を放出するといった、酸素吸蔵能(OSC)を發揮することができる。したがって、セリウム-ジルコニウム複合酸化物を排気ガス浄化用触媒に含めると、触媒成分の近傍における排気ガス組成の変動が緩和され、上記の排気ガス浄化をより効率的に進行させることができる。

【0005】これに加えて、セリウム-ジルコニウム複合酸化物の酸素吸収に伴って、かなりの発熱が生じるため、この発熱をエンジン始動時の触媒の暖機に利用し、触媒活性の開始時期を早めることができる。このため、セリウム-ジルコニウム複合酸化物は、排気ガス浄化用触媒の助触媒として使用されている。かかるセリウム-ジルコニウム複合酸化物の先行技術としては、特開平10-194742号公報、特開平6-279027号公報等がある。

【0006】

【発明が解決しようとする課題】しかるに、こうしたセリウム-ジルコニウム複合酸化物は、一般に、約1000℃以上の高温に長期間曝されること、OSC能の低下を来とし、耐久性が十分ではないという問題がある。したがって、本発明は、高温下での耐久性が改良され、安定したOSC能を有するセリウム-ジルコニウム複合酸化物を提供することを目的とする。

【0007】

【課題を解決するための手段】上記の目的は、セリウム-ジルコニウム複合金属酸化物であって、前記複合金属材料中の全金属モル数を基準に、CeとZrの合計モル数が少なくとも85%であり、Ce/Zrのモル比が1/9~9/1であり、かつ前記複合金属酸化物の等電点が3.5を上回ることを特徴とするセリウム-ジルコニウム複合金属酸化物によって達成される。

【0008】即ち、本発明は、特定の組成を有するセリウム-ジルコニウム複合金属酸化物であって、とりわけ、3.5を上回る等電点を有することを特徴とするセリウム-ジルコニウム複合金属酸化物である。

【0009】この「等電点」は、スラリー中の粒子の電気泳動に基づいて測定される特性値であって、本発明で規定する方法において、CeO₂の等電点は2.4であり、ZrO₂の等電点は4.0である。即ち、本発明のセリウム-ジルコニウム複合金属酸化物は、CeO₂とZrO₂の双方を含みながら、ZrO₂に近い等電点を有することを特徴とする。

【0010】かかる等電点として、本発明のセリウム-

3

ジルコニウム複合金属酸化物は、 CeO_2 と ZrO_2 の組成が同等の従来技術のセリウム-ジルコニウム複合金属酸化物よりも顕著に高い値を有する。また、かかるセリウム-ジルコニウム複合金属酸化物にPtを担持してなる排気ガス浄化用触媒の耐久性性能は、従来技術のそれよりも顕著に改良される。

【0011】これらのことから、本発明のセリウム-ジルコニウム複合金属酸化物は、それを構成する粒子が、外側が主として ZrO_2 、内側が主として CeO_2 からなる図1のような状態を呈し、こうした状態は、 ZrO_2 に特に希土類金属から選択された少量の元素が共存するときに安定化されるものと考えられる。即ち、本発明は、別な局面において、セリウム-ジルコニウム複合金属酸化物であって、前記複合金属酸化物中の全金属モル数を基準に、CeとZrの合計モル数が少なくとも85%であり、 CeO_2 を核とし、その核の周りに ZrO_2 が存在することを特徴とするセリウム-ジルコニウム複合金属酸化物である。

【0012】 ZrO_2 と CeO_2 がこのような存在形態を呈することにより、耐熱性の高い ZrO_2 がセリウム-ジルコニウム複合金属酸化物の粒子の形態を保持し、それによって、内側の CeO_2 、及び/又は内側と外側の境界領域の CeO_2 - ZrO_2 が経時的に安定してOSC能を発揮することができるものと推定される。なお、図1は、あくまでも模式的な説明図であって、本発明を限定するものではない。

【0013】

【発明の実施の形態】本発明は、セリウム-ジルコニウム複合金属酸化物であって、前記複合金属酸化物中の全金属モル数を基準に、CeとZrの合計モル数が少なくとも85%であり、Ce/Zrのモル比が1/9~9/1であり、かつ前記複合金属酸化物の等電点が3.5を上回ることを特徴とし、より好ましくは、前記Ce/Zrのモル比が3/7~7/3であり、前記等電点が3.8~5.0である。本発明において、「等電点」とは、JIS規格R1638に記載の電気泳動顕微鏡法の一つであるストップウォッチ法によって測定される値と定義する。

【0014】また、「セリウム-ジルコニウム複合金属酸化物」とは、少なくともCeとZrを含み、さらに別な「金属」を含むことができる酸化物である。このさらに別な「金属」は、s-ブロック金属、d-ブロック金属、p-ブロック金属、f-ブロック金属から広範囲に選択することができ、具体的には、ナトリウム(Na)、カリウム(K)、マグネシウム(Mg)、カルシウム(Ca)、バリウム(Ba)、ストロンチウム(Sr)、ランタン(La)、イットリウム(Y)、セリウム(Ce)、プラセオジウム(Pr)、ネオジウム(Nd)、サマリウム(Sm)、ユウロビウム(Eu)、ガドリニウム(Gd)、チタン(Ti)、錫(Sn)、ジ

4

ルコニウム(Zr)、マンガン(Mn)、鉄(Fe)、コバルト(Co)、ニッケル(Ni)、クロム(Cr)、ニオブ(Nb)、銅(Cu)、バナジウム(V)、モリブデン(Mo)、タングステン(W)、亜鉛(Zn)、アルミニウム(Al)、ケイ素(Si)及びタンタル(Ta)等であることができる。

【0015】好ましくは、上記のさらに別な「金属」は、La、Y、Ce、Pr、Nd、Sm、Eu、Gd等の希土類金属の少くとも1種であり、セリウム-ジルコニウム複合金属酸化物中の全金属モル数を基準に、15モル%未満の量で含まれる。「金属」がこれらの希土類金属の場合、核の周りの ZrO_2 が特に安定化されるものと考えられる。

【0016】かかるセリウム-ジルコニウム複合金属酸化物は、好ましくは、セリウム源としてセリアゾルを用いて製造され、セリアゾル、及びジルコニウム化合物溶液又はジルコニアゾル、及び好ましくはさらに別な「金属」の金属化合物溶液又はゾルを所定の割合で混合して懸濁液を調製した後、乾燥・焼成することによって得ることができる。

【0017】ここで、「セリアゾル」、「ジルコニアゾル」等の「ゾル」とは、液体の特に水に分散した酸化物又は水和物のコロイドであって、焼成してセリア、ジルコニア等の金属酸化物を生成する物質を意味し、具体的には、セリウム又はジルコニウム等のアルコキシド、アセチルアセトナト、酢酸塩、硝酸塩等を溶液中で加水分解等して得られた物質が例示される。また、「ジルコニウム化合物溶液」には、オキシ硝酸ジルコニウム $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ 、塩化ジルコニウム ZrCl_4 等の水溶液が例示される。

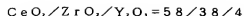
【0018】焼成は、例えば、600~900℃の大気雰囲気中で数時間加熱する条件が適切である。このようにして得られたセリウム-ジルコニウム複合金属酸化物を必要により粉碎工程に供した後、白金、パラジウム、ロジウム等の貴金属が担持されて、排気ガス浄化用触媒が調製されることができ、かかる排気ガス浄化用触媒は、約1000℃の温度に曝されてもOSC能が有意に劣化せずに、安定した高い排気ガス浄化性能を発揮することができる。以下、実施例によって本発明をより具体的に説明する。

【0019】

【実施例】実施例1

193.33gのセリアゾル(CeO_2 として15質量%、多水化学製、ニードラルU-15)に、100gのイオン交換水に41.16gのオキシ硝酸ジルコニウムと6.48gの硝酸イットリウムを溶解させた溶液を添加して攪拌し、均一な懸濁液を作成した。この懸濁液を120℃×24時間の加熱に供して水を蒸発させた後、700℃×5時間の焼成に供し、下記の組成(質量比)：

50



の本発明のセリウム-ジルコニウム複合金属酸化物を得た。

【0020】次いで、この複合酸化物の50gを300gのイオン交換水に分散させたスラリーを作成し、このスラリーにジニトロジアンミン白金錯体の水溶液(Pt濃度4.4質量%)を11.36g加えて2時間攪拌した。次いで、このスラリーを120℃×24時間の加熱に供して水を蒸発させた後、500℃×2時間の焼成に供し、本発明のセリウム-ジルコニウム含有複合酸化物に1質量%のPtを担持した本発明の排気ガス浄化用触媒を得た。

【0021】実施例2

193.33gの上記のセリアゾルに、50gのイオン交換水に6.48gの硝酸イットリウムを溶解させた溶液と、ジルコニアゾル(ZrO_2 として20質量%、第一希元素化学工業製、ジルコニアHA)を95g添加して攪拌し、均一な懸濁液を作成した。

【0022】次いで、実施例1と同様にして、この懸濁液から水を蒸発させた後、700℃×5時間の焼成に供し、下記の組成(質量比): $\text{CeO}_2/\text{ZrO}_2/\text{Y}_2\text{O}_3 = 58/38/4$ の本発明のセリウム-ジルコニウム複合金属酸化物を得た。次いで、実施例1と同様にして、ジニトロジアンミン白金錯体を用いてこの複合酸化物に1質量%のPtを担持し、本発明の排気ガス浄化用触媒を得た。

【0023】実施例3

193.33gの上記のセリアゾルに、50gのイオン交換水に6.48gの硝酸イットリウムを溶解させた溶液と、ジルコニアゾル(ZrO_2 として12.5質量%、第一希元素化学工業、ジルコニアAC7)を154.5g添加して攪拌し、均一な懸濁液を作成した。

【0024】次いで、実施例1と同様にして、この懸濁液から水を蒸発させた後、700℃×5時間の焼成に供し、下記の組成(質量比):

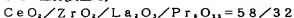


の本発明のセリウム-ジルコニウム複合金属酸化物を得た。次いで、実施例1と同様にして、ジニトロジアンミン白金錯体を用いてこの複合酸化物に1質量%のPtを担持し、本発明の排気ガス浄化用触媒を得た。

【0025】実施例4

193.33gの上記のセリアゾルに、300gのイオン交換水に34.66gのオキシ硝酸ジルコニウム、3.99gの硝酸ランタン、及び8.94gの硝酸プラセオジウムを溶解させた溶液を添加して攪拌し、均一な懸濁液を作成した。

【0026】次いで、実施例1と同様にして、懸濁液から水を蒸発させた後、700℃×5時間の焼成に供し、下記の組成(質量比):

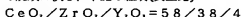


の本発明のセリウム-ジルコニウム複合金属酸化物を得た。次いで、実施例1と同様にして、ジニトロジアンミン白金錯体を用いてこの複合酸化物に1質量%のPtを担持し、本発明の排気ガス浄化用触媒を得た。

【0027】比較例1

500gのイオン交換水に73.165gの硝酸セリウム、41.16gのオキシ硝酸ジルコニウム、及び6.48gの硝酸イットリウムを溶解させた溶液を作成した。次いで、この溶液に濃度1モル/リットルのアンモニア水を滴下して、pHを約9に調節し、共沈により沈殿物を生じさせた。

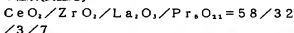
【0028】次いで、実施例1と同様にして、この沈殿物を含む溶液から水を蒸発させた後、700℃×5時間の焼成に供し、下記の組成(質量比):



の比較例のセリウム-ジルコニウム複合金属酸化物を得た。次いで、実施例1と同様にして、ジニトロジアンミン白金錯体を用いてこの複合酸化物に1質量%のPtを担持し、比較例の排気ガス浄化用触媒を得た。

【0029】比較例2

500gのイオン交換水に73.17gの硝酸セリウム、34.66gのオキシ硝酸ジルコニウム、3.99gの硝酸ランタン、及び8.94gの硝酸プラセオジウムを溶解させた溶液を調製した。次いで、比較例1と同様にして、この溶液から共沈により沈殿物を生じさせ、水を蒸発させた後、700℃×5時間の焼成に供し、下記の組成(質量比):

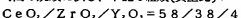


の比較例のセリウム-ジルコニウム複合金属酸化物を得た。次いで、実施例1と同様にして、ジニトロジアンミン白金錯体を用いてこの複合酸化物に1質量%のPtを担持し、比較例の排気ガス浄化用触媒を得た。

【0030】比較例3

500gのイオン交換水に29gの酸化セリウム粉末を分散させ、次いで、200gのイオン交換水に41.16gのオキシ硝酸ジルコニウムと6.48gの硝酸イットリウムを溶解させた溶液を添加して攪拌し、スラリーを調製した。次いで、このスラリーに、比較例1と同様にしてアンモニア水を滴下して、pHを約9に調節し、ジルコニウムとイットリウムを含む沈殿物を生じさせた。

【0031】次いで、水を蒸発させた後、700℃×5時間の焼成に供し、下記の組成(質量比):



の比較例のセリウム-ジルコニウム複合金属酸化物を得た。次いで、比較例1と同様にして、ジニトロジアンミン白金錯体を用いてこの複合酸化物に1質量%のPtを担持し、比較例の排気ガス浄化用触媒を得た。

【0032】一等電位の測定—

実施例1～4と比較例1～3の各セリウム-ジルコニウム複合金属酸化物について、JIS規格R1638に記載の電気泳動顕微鏡法の1つであるストップウォッチ法に準じて、等電点を測定した。この結果を表1にまとめて示す。また、図2に、実施例1と比較例1のセリウム-ジルコニウム複合金属酸化物、及びCeO₂粉末とZrO₂粉末について、上記の測定方法において等電点を求めるために測定されたpHとゼータ電位の関係を示す。

【0033】これらの結果から、実施例と比較例のセリウム-ジルコニウム複合金属酸化物の等電点に明らかな相違があり、実施例では、ZrO₂粉末に近い等電点を示し、比較例では、CeO₂粉末に近い等電点を示すことが分かる。しかるに、実施例1～3と比較例1及び3、実施例4と比較例2では、セリウム-ジルコニウム複合金属酸化物の組成は同等であるため、これらの相違は、CeO₂とZrO₂の存在形態に由来するものと判断され、実施例では、図1に示すように、CeO₂を核としてその周りにZrO₂が存在するために、ZrO₂粉末に近い等電点を示すものと考えられる。

*20

〔表1〕評価用のガス組成

	H ₂ (%)	O ₂ (%)	NO (ppm)	CO (%)	C ₂ H ₄ (ppm)	H ₂ (%)	O ₂ (%)	H ₂ O (%)
リッチガス	バランス	10	2200	2.80	2500	0.27	0.77	10
リーンガス	バランス	10	2200	0.81	2500	0	1.7	10

【0038】

*【0034】—触媒性能評価—

実施例1～4と比較例1～3の各排気ガス浄化用触媒を圧縮・解砕して、直径約2mmのペレットにした各2.0gについて、触媒性能を評価した。耐久性の改良効果を把握するため、各排気ガス浄化用触媒を1000℃×3時間の耐久処理に供した後、触媒性能を評価した。

【0035】評価条件は、OSC能の差異が結果に現れるように、表1に示す組成のリッチガス/リーンガスが1分毎に切り替わる条件とし、触媒床温度を10℃/分の速度で400℃まで昇温させながらC₂H₄(HC)、NO、COの各成分の浄化率を測定した。触媒性能は、これらの成分が50%浄化される温度を指標とした。この結果を表2にまとめて示す。

【0036】

【発明の効果】高温下での耐久性が改良され、安定したOSC能を有するセリウム-ジルコニウム複合酸化物を提供することができる。

【0037】

〔表1〕

〔表2〕

(表2) 触媒性能と等電点の測定結果

	組 成	質量比	HC	NO	CO	等電点
実施例 1	Ce-Zr-Y-O	58/38/4	234	286	180	4.2
実施例 2	Ce-Zr-Y-O	58/38/4	253	288	221	3.9
実施例 3	Ce-Zr-Y-O	58/38/4	263	301	216	4.1
実施例 4	Ce-Zr-La-Pr-O	58/32/3/7	245	270	201	4.0
比較例 1	Ce-Zr-Y-O	58/38/4	260	308	242	2.5
比較例 2	Ce-Zr-La-Pr-O	58/32/3/7	269	303	253	2.2
比較例 3	Ce-Zr-Y-O	58/38/4	302	366	299	3.3

【図面の簡単な説明】

【図1】本発明のセリウム-ジルコニウム複合金属酸化物のモデル図である。

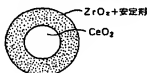
10* 【図2】等電点の測定におけるpHとゼータ電位の関係を示すグラフである。

*

【図1】

図1

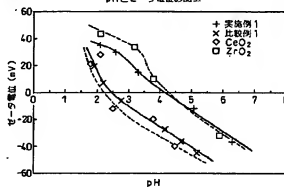
本発明のセリウム-ジルコニウム複合金属酸化物のモデル図



【図2】

図2

pHとゼータ電位の関係



フロントページの続き

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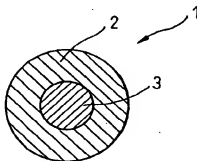
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(54) **A method for preparing metal oxide particles and an exhaust gas purifying catalyst**

(57) The present invention relates to metal oxide particles having cores comprising larger molar amounts of zirconia than of ceria, and surface layers comprising larger molar amounts of ceria than of zirconia. Further, the present invention relates to a method for preparing the particles. The method comprises preparing a solution comprising zirconia sol and ceria sol, adjusting the

pH of the solution within ± 0.5 on the basis of the isoelectric point of zirconia, and aggregating zirconia and then aggregating ceria around the aggregated zirconia from the solution to make aggregates. Furthermore, the present invention relates to an exhaust gas purifying catalyst comprising the metal oxide particles, and a noble metal carried by the metal oxide particles.

Fig.1**EP 1 415 956 A2**

Description

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The present invention relates to a catalyst for purifying the contents of exhaust gas from an internal combustion engine, and metal oxide particles suitable as a carrier for an exhaust gas purifying catalyst and a method for preparing this.

2. Description of the Related Art

[0002] Exhaust gas from an internal combusting engine such as an automobile engine comprises nitrogen oxide (NO_x), carbon monoxide (CO), hydrocarbon (HC) and etc. These contents of the exhaust gas can be purified by the use of an exhaust gas purifying catalyst which oxidizes CO and HC while reduce NO_x . A representative exhaust gas purifying catalyst includes a three way catalyst which comprises porous metal oxide carrier such as γ -alumina and a noble metal such as platinum (Pt), Rhodium (Rh) and/or Palladium (Pd) carried thereon.

[0003] It is necessary that an internal combustion engine is driven at stoichiometric air/fuel ratio (stoichiometry) in order for the three way catalyst to achieve effective oxidation of CO and HC as well as reduction of NO_x . In the case that the internal combustion engine is driven at excess oxygen atmosphere (lean) or at excess fuel atmosphere (rich), the three-way catalyst cannot demonstrate its purification ability as the oxygen concentration in the exhaust gas becomes outside the range of the optimum oxygen concentration for the three-way catalyst.

[0004] It is well known that a material having an oxygen storage capacity (OSC) is used with an exhaust gas purifying catalyst. OSC means a capacity enabling storing oxygen at the high oxygen concentration and releasing oxygen at the low oxygen concentration. OSC is useful to buffer the change of oxygen concentration in exhaust gas and thereby enhances the exhaust gas purifying ability of the three way catalyst. A representative material having OSC is ceria (CeO_2). Ceria has not only OSC but also large affinity with noble metal carried thereon. Therefore, the ceria is also useful to prevent particle growth (sintering) of the noble metal carried thereon. Methods for preparing mixed metal oxide of ceria and zirconia have been developed to provide materials having high heat resistivity as ceria has small specific surface area and low heat resistivity. Regarding the prior arts, refer to Japanese Unexamined Patent Publication No. 8-103650, 8-109020, 8-109021, 2000-319019, 2001-89143 and etc.

[0005] According to the prior arts, as both ceria and zirconia exist on the surface of the mixed metal oxide comprising uniformly mixed ceria and zirconia, a noble metal carried by the mixed metal oxide randomly deposits on both ceria and zirconia surface. Therefore, in the prior arts, there is a problem that an affinity between the mixed metal oxide and noble metal is lowered, the noble metal is sintered and, then, the catalyst loses its ability to purify exhaust gas.

[0006] That is, the previous catalysts comprising a cerium-zirconium mixed metal oxide lose OSC, and an ability to purify exhaust gas, by the sintering of noble metal on their surface, particularly when they are exposed to a high temperature of 1000°C or more for a long time.

[0007] Therefore, there remains a need for an exhaust gas purifying catalyst which maintains a heat resistivity of mixed metal oxide, has high affinity to a noble metal to maintain OSC, and only slightly lose its ability to purify exhaust gas after being exposed to a high temperature. Further, there remains a need for a method for preparing a metal oxide suitable for the exhaust gas purifying catalyst.

BRIEF SUMMARY OF INVENTION

[0008] In one aspect, the present invention is an exhaust gas purifying catalyst. The exhaust gas purifying catalyst comprises metal oxide particles comprising ceria and zirconia; and noble metal carried by the metal oxide particles, wherein the metal oxide particles have cores comprising larger molar amounts of zirconia than of ceria, and surface layers comprising larger molar amounts of ceria than of zirconia. The exhaust gas purifying catalyst may then have a superior heat resistivity and a superior ability to purify exhaust gas after enduring test at high temperature.

[0009] The metal oxide particles may have a mean particle diameter of 500 nm or less, 200 nm or less, 100 nm or less, or 50 nm or less, with 50 nm or less being preferred.

[0010] The catalyst may be used for purifying exhaust gas from an internal combustion engine such as an automobile engine.

[0011] The catalyst may be used at the temperature of 1,000°C or more.

[0012] The molar ratio of Zr:Ce in the metal oxide particles may be 1:0.5 to 0.5:1, 1:0.8 to 0.8:1, or about 1:1, with about 1:1 being preferred.

[0013] The metal oxide particles may further comprise one or more metal oxides other than ceria and zirconia.

[0014] The molar ratio of (Zr and Ce):(the other metals) may be 5:1 to 20:1, 8:1 to 10:1, or about 9:1.

[0015] The ceria may cover more than 80 mol%, 90 mol%, 95 mol% or 98 mol% of the surfaces of the metal oxide particles, and preferably substantially all of the metal oxide surface, as measured by the transmission electron microscope (TEM) and energy dispersive X-ray analyzer (EDX).

[0016] The zirconia may form more than 80 mol%, 90 mol%, 95 mol% or 98 mol% of the cores of metal oxide particles, and preferably substantially all of the cores, as measured by the transmission electron microscope (TEM) and energy dispersive X-ray analyzer (EDX).

[0017] In another aspect, the present invention is metal oxide particles having cores comprising larger molar amounts of zirconia than of ceria, and surface layers comprising larger molar amounts of ceria than of zirconia.

[0018] The metal oxide particles may carry a noble metal.

[0019] In another aspect, the present invention is a method for preparing metal oxide particles in which the metal oxide particles have cores comprising larger molar amounts of zirconia than of ceria, and surface layers comprising larger molar amounts of ceria than of zirconia. The method comprises preparing a solution comprising zirconia sol and ceria sol, adjusting the pH of the solution within ± 0.5 on the basis of the isoelectric point of zirconia, and aggregating a zirconia and then aggregating ceria around the aggregated zirconia from the solution to make aggregates. According to the method, the metal oxide particles of the present invention are easily prepared, and the prepared metal oxide particles may have a very small mean particle diameter and large specific surface area.

[0020] The metal oxide particles may have a mean particle diameter of 500 nm or less, 200 nm or less, 100 nm or less, or 50 nm or less, with 50 nm or less being preferred.

[0021] The molar ratio of Zr:Ce in the metal oxide particles may be 1:0.5 to 0.5:1, 1:0.8 to 0.8:1, or about 1:1, with about 1:1 being preferred.

[0022] These and other objects, feature and advantages of the present invention will become apparent upon reading of the following detailed description along with the accompanied drawings.

BRIEF DESCRIPTION OF DRAWING

[0023]

Fig. 1 is a schematic sectional view of the metal oxide particle of the present invention that can be used for a catalyst of the present invention. However, it is not necessary for the core 2 and surface layer 3 to be adjacent.

DETAILED DESCRIPTION OF INVENTION

[0024] The inventor of the present invention found that an exhaust gas purifying catalyst comprising metal oxide particles 1 having zirconia-rich core 2 and ceria-rich surface layer 3, and a noble metal carried by the metal oxide particles, shows an improved ability to purify exhaust gas even after an endurance test, and conceived the catalyst of the present invention.

[0025] The inventor of the present invention found that the metal oxide particles can be prepared by preparing a solution comprising zirconia sol and ceria sol, adjusting the pH of the solution around the isoelectric point of zirconia, aggregating and precipitating a metal oxide from the solution, and firing the aggregate. Thus prepared metal oxide particles have zirconia-rich core and ceria-rich surface layers, and very small particle sizes.

[0026] The exhaust gas purifying catalyst according to the present invention comprises metal oxide particles as a substrate and a noble metal carried thereby, and is characterized in that the metal oxide particles have cores comprising larger molar amounts of zirconia than of ceria and surface layers comprising larger molar amounts of ceria of zirconia.

[0027] It is also possible to prepare metal oxide particles having cores comprising larger molar amounts of zirconia than of ceria and surface layers comprising larger molar amounts of ceria than of zirconia by a method comprising mixing zirconia particle and ceria sol, aggregating ceria around the zirconia particle and firing it. However, zirconia particles used in this method generally have a mean diameter of a few micrometers or more and, then, the metal oxide particles obtained by aggregating ceria around the zirconia particles and firing it also have a mean particle diameter of a few micrometer or more. The large particles comprising ceria and zirconia such as particles having a mean particle diameter of a few micrometer or more hardly improves the heat resistivity of ceria for OSC (effect of improving heat resistivity) provided by a cerium-zirconium mixed metal oxide, even if the metal oxide particles comprise ceria and zirconia.

[0028] The method for preparing metal oxide particle of the present invention comprises adjusting a pH of the solution comprising zirconia sol and ceria sol to around the isoelectric point of zirconia sol, and aggregating the sols into metal oxide particles. The metal oxide particles prepared by this method are very small, have large specific surface areas, and provide an effect of improving the heat resistivity of ceria by the use of zirconia.

[0029] The method for preparing metal oxide particles of the present invention is further described at the following.

The term "sol" in the zirconia sol or ceria sol means a colloid of metal oxide or metal hydride dispersed in liquid, especially water. Zirconia or ceria may be provided by removing liquid from sol and being fired. For example, the zirconia sol or ceria sol may be obtained by hydrating or condensing alkoxide, acetylacetonate, acetate, nitrate and etc. of zirconium or cerium in a solution. A zirconia sol and ceria sol are well known and commercially available.

[0030] Although the method of the present invention uses a solution comprising zirconia sol and ceria sol as raw material, the solution may further comprise salt and/or sol of metals other than Ce and Zr, and any the other material. The metals other than Ce and Zr may be selected from the group consisting of s-block metals, d-block metals, p-block metals, and f-block metals. More specially, the metals other than Ce and Zr include Na, K, Mg, Ca, Ba, Sr, La, Y, Pr, Nd, Sm, Eu, Gd, Ti, Sn, Mn, Fe, Co, Ni, Cr, Nb, Cu, V, Mo, W, Zn, Al, Si and Ta. Preferably, the metals other than Ce and Zr include rare earth metals such as one or more metals selected from the group consisting of La, Y, Pr, Nd, Sm, Eu and Gd, especially one or more metals selected from the group consisting of La, Y and Pr.

[0031] Specially, a metal salt such as lanthanum nitrate and praseodymium nitrate, and/or sol compound such as yttria sol may be added to zirconia sol and ceria sol. A metal oxide formed from raw material comprising salt and/or sol of rare earth metal has high heat resistivity and shows a small reduction of OSC after being exposed to a high temperature.

[0032] The mixing ratio of zirconia sol, ceria sol, and salt and/or sol of the other metals may be optionally determined. It is, however, preferable to use about the same amounts of Zr and Ce (e.g. molar ratio of Zr:Ce:the other metals is 45:45:10) in order to maintain heat resistivity.

[0033] According to the method for preparing metal oxide of the present invention, the pH of the solution comprising zirconia sol and ceria sol ("raw sol solution") is adjusted to about the isoelectric point of zirconia, and aggregates sols into particles.

[0034] The isoelectric point of zirconia can be determined by a stopwatch method which belongs to an electrophoresis-microscope method (c.f. JIS (Japanese Industrial Standard) R1638). The isoelectric point of the zirconia may be determined for zirconia obtained by drying and firing the raw zirconia sol of same lot as the zirconia sol to be used in examples.

[0035] The pH of the raw material may be adjusted by addition of any kind of acid or base, with mineral acid such as nitric acid and/or hydrogen chloride being preferred as an acid, and aqueous ammonia and/or sodium hydroxide being preferred as a base. A commercially available metal oxide sol solution has a pH that rather differs from the isoelectric point of zirconia sol in order to prevent aggregation, precipitation and solution of metal oxide sol. Therefore, an acid is generally added to a basic zirconia sol solution for the method of the present invention.

[0036] It is most preferable to precisely adjust the pH of a raw sol solution to the isoelectric point of zirconia, but it is practically very difficult. Therefore, it is preferable to adjust the pH of the raw sol solution within ± 0.5 , more preferably within ± 0.2 on the basis of the isoelectric point of the zirconia sol. The pH of the raw sol solution may be adjusted by adding an acid or a base to the raw sol solution while measuring pH of the raw sol solution by a pH meter. Alternatively, the pH of the raw sol solution may be adjusted by sampling the raw sol solution to predetermine an amount of acid or base required for adjusting pH of the raw sol solution, and then adding the predetermined amount of acid or base to the bulk raw sol solution.

[0037] A solvent for a raw sol solution is generally water, and may comprise an organic solvent such as alcohol and acetylacetone, if required. The solvent may be removed and dried out from a raw sol solution by any method and at any temperature, e.g. the solvent may be removed and dried out by introducing the raw sol solution into an oven at the temperature of 120°C.

[0038] Metal oxide particles may be prepared by removing solvent from a raw sol solution and firing the dried raw material. The firing step may be performed at a temperature generally used for metal oxide synthesis, e.g. 500°C or more such as 500 to 1,000°C.

[0039] The metal oxide particles prepared by the method of the present invention have rather smaller diameters and larger specific surface areas than those prepared by the well method wherein sintered metal oxide is milled. Therefore, the metal oxide particles prepared by the method of the present invention can carry a noble metal in a highly dispersed manner. The metal oxide particles prepared by the present invention has a diameter of 50 nm or less when a sol having a mean diameter of about 5 nm is used as a raw material, while metal oxide particles prepared by milling a bulk metal oxide have mean particle diameters of 1 μ m or more.

[0040] The metal oxide particles prepared by the method of the present invention have cores comprising a larger molar amounts of zirconia than of ceria, and surface layers comprising larger molar amounts of ceria than of zirconia. In fact, the metal oxide particle prepared by the following examples has about same isoelectric point about as that of ceria. Therefore, it is deemed that the ceria covers substantially all the surface of the metal oxide particle. The Ce and Zr distribution within the metal oxide particle obtained by the transmission electron microscope (TEM) and energy dispersive X-ray analyzer (EDX) shows that almost all metal elements at the surfaces of the particles are Ce and that almost all metal elements at the cores of the particles are Zr.

[0041] It is deemed that the method of the present invention provides a metal oxide particles having zirconia-rich

cores and ceria-rich surface layers for the following reasons:

[0042] At the isoelectric point of the zirconia, zirconia particles tend to aggregate since a zeta potential at the surface of the zirconia particles become zero, and the surfaces of the zirconia particles are electrically neutral and do not have electrical charge. At the isoelectric point of the zirconia, ceria has a positive zeta potential and positive electrical charge since ceria has higher isoelectric point than zirconia. Therefore, when the pH of a solution comprising ceria sol and zirconia sol is adjusted to the isoelectric point of zirconia, zirconia having neutral electrical potential tends to aggregate and ceria having positive potential does not tend to aggregate. At this situation, firstly zirconia is aggregated and then ceria is aggregated around the aggregated zirconia cores when the metal oxide particles are aggregated, e.g. by concentrating the solution. Therefore, the metal oxide particles prepared by the method of the present invention have zirconia-rich cores and ceria-rich surface layers.

[0043] An exhaust gas purifying catalyst may be prepared by carrying a noble metal on the above metal oxide particles. The noble metal may be carried on metal oxide particles by the any method, e.g. by soaking an aqueous solution of salt and/or complex of noble metal into the metal oxide particles, and then drying and firing the metal oxide particles. It is preferable that the metal oxide particles carry one or more noble metals selected from the group consisting of Pt, Pd, Rh, Ir and Au, more preferably one or more noble metals having high exhaust gas purification ability selected from the group consisting of Pt, Pd and Rh, even more preferably Pt. It is preferable that the metal oxide particles carry a noble metal at an amount of 0.01 to 5 wt%, more preferably 0.1 to 2 wt% on the basis of the amount of the metal oxide particles. The exhaust gas purification ability is not sufficient when the noble metal carried by the metal oxide particles is less than 0.01 wt%, while cost is increased though the exhaust gas purification ability is saturated when the noble metal carried by metal oxide particles is more than 5 wt%.

[0044] Because the metal oxide particles prepared by the method of the present invention have very small particle diameters and large specific surface areas, the noble metal carried thereon can be well-dispersed and has a small particle diameter.

[0045] The exhaust gas purifying catalyst of the present invention has a superior ability for exhaust gas purification after a high temperature endurance test and a superior heat resistivity relative to the exhaust gas purifying catalyst comprising the noble metal carried on the metal oxide particles composed of equally dispersed ceria and zirconia.

[0046] The exhaust gas purifying catalyst of the present invention is very useful for purifying an exhaust gas from an internal combustion engine such as automobile engine. The method for preparing a metal oxide particles of the present invention is very useful for preparing metal oxide particles used for an exhaust gas purifying catalyst.

[0047] The exhaust gas purifying catalyst of the present invention can be used in coatings on a monolithic substrate such as a ceramic honeycomb. The present invention is described, on the basis of examples, as follows.

EXAMPLES

[0048] The same zirconia sol as that used for following examples was dehydrated and dried to obtain ZrO_2 . The isoelectric point of the obtained ZrO_2 was determined by the stopwatch method that is one of electrophoretic microscopy methods (JIS (Japanese Industrial Standard) R1638). It was shown that the ZrO_2 has an isoelectric point of pH 4.0. Therefore, in the following examples, the value of pH 4.0 was used as isoelectric point of ZrO_2 .

[0049] In the following examples, the pH of the metal oxide sol solution is determined by a pH meter wherein the electrode of the pH meter is directly dipped into the metal oxide sol solution.

Example 1 - Preparation of Catalyst 1:

[0050] A zirconia sol comprising 10.2 wt% of ZrO_2 (TAKI CHEMICAL CO., LTD., ECOLIGHT) (111.76g) and yttria sol comprising 15 wt% of Y_2O_3 (TAKI CHEMICAL CO., LTD., Y_2O_3 sol) (6g) were added to a ceria sol comprising 15 wt% of CeO_2 (TAKI CHEMICAL CO., LTD., NEEDRAL U-15) (116g), and mixed. The resulting sol mixture had a pH of 5.8.

[0051] An aqueous nitric acid was added to the sol mixture to adjust pH of the sol mixture to pH 4.0 that is the isoelectric point of the ZrO_2 . The adjusted solution was dehydrated, and an resulting solid material was dried at 120°C for 24 hours and then fired at 700°C for 5 hours to obtain mixed metal oxide particles. The obtained mixed metal oxide particles had a specific surface area of 66.8 m²/g. To the solution consisting of water particles (300g) and the mixed metal oxide particles (30g) dispersed therein, a platinum dinitrodiamine solution (6.82g) comprising 4.4 wt% of Pt was added and stirred for two hours, and then the resulting mixture was dehydrated to obtain solid material. The obtained solid material was dried at 120°C and then fired at 500°C for two hours to obtain Catalyst 1. The Catalyst 1 had a weight ratio of CeO_2 : ZrO_2 : Y_2O_3 = 58:38:4. The Catalyst 1 consists of mixed metal oxide particles having a surface layer of CeO_2 and core of ZrO_2 and Y_2O_3 , and Pt carried thereby. The amount of Pt carried by mixed metal oxide particles was 1 wt% on the basis of the weight of the mixed metal oxide particles.

Example 2 - Preparation of Catalyst 2

[0052] Catalyst 2 was prepared according to the Example 1 except that ceria sol (193.33g), zirconia sol (156.85g), and aqueous solution (30 cc) comprising nitric lanthanum (3.99g) and nitric praseodymium (8.94g) in solution were used as the substitute for ceria sol (116g), zirconia sol (111.76g) and yttria sol (6g). The obtained Catalyst 2 had a weight ratio of $\text{CeO}_2\text{:ZrO}_2\text{:La}_2\text{O}_3\text{:Pr}_6\text{O}_{11} = 58\text{:}32\text{:}3\text{:}7$. The Catalyst 2 consists of mixed metal oxide particles having a surface layer of CeO_2 and Pt carried thereby. The amount of Pt carried by mixed metal oxide particles was 1 wt% on the basis of the weight of the mixed metal oxide particles. The mixed metal oxide had a specific surface area of 69.6 m^2/g before carrying Pt.

Comparative Example 1 - Preparation of Catalyst 3

[0053] A same ceria sol (200g) as that used in example 1 was dried at 120°C. The resulting solid material was fired at 700°C for five hours to obtain CeO_2 . The obtained CeO_2 had a specific surface area of 23.4 m^2/g . To the CeO_2 (30g), water (300g) and platinum dinitrodiamine solution (6.82g) comprising 4.4 wt% of Pt were added, and stirred for two hours to obtain a mixture. The solid material obtained after drying this mixture at 120°C was fired at 500°C for two hours to obtain Catalyst 3.

Comparative Example 2 - Preparation of Catalyst 4

[0054] Cerium nitrate (73.165g), zirconium oxynitrate (41.16g) and yttrium nitrate (6.48g) was added to water (500g), and mixed to obtain uniform solution. While the pH of the solution was measured by a pH meter, an aqueous ammonia was added to the solution to adjust pH of the solution to 9 and provide a precipitate. A solid material obtained after drying this solution at 120°C was fired at 500°C for two hours to obtain mixed metal oxide particles. To a solution comprising the mixed metal oxide particles (50g) dispersed in water (300g), platinum dinitrodiamine solution (11.36g) comprising 4.4 wt% of Pt was added and stirred for two hours to obtain a mixture. This mixture was dried at 120°C, and fired at 500°C for two hours to obtain Catalyst 4. The obtained Catalyst 4 had a weight ratio of $\text{CeO}_2\text{:ZrO}_2\text{:Y}_2\text{O}_3 = 58\text{:}38\text{:}4$. An amount of Pt carried by mixed metal oxide was 1 wt% on the basis of the weight of the mixed metal oxide particles.

Comparative Example 3 - Preparation of Catalyst 5

[0055] A cerium nitrate (73.17g), zirconium oxynitrate (34.66g), lanthanum nitrate (3.99g) and praseodymium nitrate (8.94g) were added to water (500g), and mixed to obtain uniform solution. While the pH of the solution was measured by a pH meter, aqueous ammonia was added to the solution to adjust pH of the solution to 9 and provide precipitate. A solid material obtained after drying this solution at 120°C was fired at 700°C for five hours to obtain mixed metal oxide particles. To this mixed metal oxide (30g), water (300g) and platinum dinitrodiamine solution (6.82g) comprising 4.4 wt% of Pt were added and stirred for two hours to obtain a mixture. The solid material obtained after drying this mixture at 120°C was fired at 500°C for two hours to obtain Catalyst 5. The obtained Catalyst 5 had a weight ratio of $\text{CeO}_2\text{:ZrO}_2\text{:La}_2\text{O}_3\text{:Pr}_6\text{O}_{11} = 58\text{:}32\text{:}3\text{:}7$. An amount of Pt carried on the mixed metal oxide particles was 1 wt% on the basis of the weight of the mixed metal oxide particles.

Evaluation of the Catalysts

[0056] The mean particle diameters of the mixed metal oxide particles prepared in above examples and comparative examples were determined by measuring particle diameters of the randomly sampled 100 particles by TEM and calculating mean values of the particle diameter for each examples and comparative examples.

[0057] 1 mm square pellets made of Catalysts 1 to 5 in above examples and comparative examples were evaluated for exhaust gas purifying ability. Catalysts 1 to 5 were evaluated for specific surface area and particle size of Pt carried thereby. The specific surface area was evaluated by BET one point method. The diameter of the carried Pt was evaluated by CO pulse method. In the CO pulse method for determining Pt particle diameter, an amount of CO absorbed by CeO_2 family oxide before carrying Pt was deduced from an amount of CO absorbed by Catalysts 1 to 5 for CO pulse method as CeO_2 also has a CO absorbing ability.

[0058] A rich gas and a lean gas were used as a model exhaust gas for evaluating an exhaust gas purifying ability of catalyst. The compositions of the rich and lean gases are shown in table 1.

[Table 1]

[0059]

Table 1

	N ₂ (%)	CO ₂ (%)	NO (ppm)	CO (%)	C ₃ H ₆ (ppmC)*2	H ₂ (%)	O ₂ (%)	H ₂ O (%)
rich gas	balance *1	10	2200	2.80	2500	0.27	0.77	10
lean gas	balance *1	10	2200	0.81	2500	0	1.7	10

*1 N₂ is the rest of the contents.

*2 The unit is based on an amount of carbon atoms.

Evaluation Procedure

[0060] Firstly, an enduring test was conducted wherein the catalysts were contacted with a model gas at 800°C for five hours. The model gas consisted of the rich gas and lean gas which were switched every minute.

[0061] After enduring test, while rich and lean gases were switched at 1 Hz, the model gas was heated, and the temperature at which the C₃H₆ content in model gas after passing the catalyst was reduced to less than 50% was determined and considered as HC-T50(°C). The lower the value of HC-T50(°C), the higher the exhaust gas purification ability of the catalyst. The results obtained for Catalysts 1 to 5 are listed in table 2.

[Table 2]

[0062]

Table 2

Catalyst to be evaluated (Ex.No.)	Metals whose oxides constitute catalysts *1	Weight ratio of the oxide of above metal	Specific surface area	Mean particle size of mixed metal oxide	Particle size of Pt	HC-T50
			(m ² /g)	(nm)	(nm)	(°C)
Catalyst 1 (Example 1)	Ce/Zr/Y Ce/Zr/Y	58/38/4	52	32	3.8	224
Catalyst 2 (Example 2)	Ce/Zr/la/Pr	58/32/3/7	59	26	3.2	222
Catalyst 3 (Comparative Example 1)	Ce	100	8	1260	6.2	325
Catalyst 4 (Comparative Example 2)	Ce/Zr/Y	58/38/4	36	325	9.3	298
Catalyst 5 (Comparative Example 3)	Ce/Zr/la/Pr	58/32/3/7	28	490	9.9	293

[0063] From the results listed in table 2, it is apparent that Catalyst 1 prepared in example 1 has a smaller Pt particle size, lower HC-50 value and superior ability as an exhaust gas purifying catalyst than Catalyst 4 prepared in comparative example 2 though Catalyst 1 has same composition as Catalyst 4. Further, it is apparent that Catalyst 2 prepared in example 2 has a smaller Pt particle size, lower HC-50 value and superior ability as an exhaust gas purifying catalyst than Catalyst 5 prepared in comparative example 3 though Catalyst 2 has same composition as Catalyst 5. Catalyst 3 prepared in comparative example 1 has a moderate Pt particle size among Catalysts 1 to 5, and large affinity between Pt and CeO₂. However, Catalyst 3 is not preferred, as an exhaust gas purifying catalyst, as Catalyst 3 has smaller specific surface area and lower heat resistivity of CeO₂, and also has largest HC-T50 value.

[0064] Although the present invention has been fully described by way of example with reference to the accompa-

nying drawings, it is to be understood that various changes and modifications will be apparent to those skilled in the art. Therefore, unless otherwise such changes and modifications depart from the scope of the present invention hereinafter defined, they should be construed as being included therein.

[0065] The present invention relates to metal oxide particles having cores comprising larger molar amounts of zirconia than of ceria, and surface layers comprising larger molar amounts of ceria than of zirconia. Further, the present invention relates to a method for preparing the particles. The method comprises preparing a solution comprising zirconia sol and ceria sol, adjusting the pH of the solution within ± 0.5 on the basis of the isoelectric point of zirconia, and aggregating zirconia and then aggregating ceria around the aggregated zirconia from the solution to make aggregates. Furthermore, the present invention relates to an exhaust gas purifying catalyst comprising the metal oxide particles, and a noble metal carried by the metal oxide particles.

Claims

1. An exhaust gas purifying catalyst comprising:

metal oxide particles comprising ceria and zirconia; and
a noble metal carried by said metal oxide particles,

wherein said metal oxide particles have cores comprising larger molar amounts of zirconia than of ceria, and surface layers comprising larger molar amounts of ceria than of zirconia.

2. The catalyst according to claim 1 wherein the metal oxide particles have a mean particle diameter of 500 nm or less.

3. The catalyst according to claim 1 for purifying exhaust gas from an internal combustion engine.

4. The catalyst according to claim 1 used at the temperature of 1,000°C or more.

5. The catalyst according to claim 1 wherein the molar ratio of Zr:Ce in the metal oxide particles is 1:0.5 to 0.5:1.

6. The catalyst according to claim 1 further comprising one or more metal oxides other than ceria and zirconia.

7. The catalyst according to claim 1 wherein the molar ratio of (Zr and Ce):(the other metals) is 5:1 to 20:1.

8. The catalyst according to claim 1 wherein the ceria covers more than 80 mol% of the surface of the metal oxide particles, as measured by the transmission electron microscope and energy dispersive X-ray analyzer.

9. The catalyst according to claim 1 wherein the zirconia composes more than 80 mol% of the cores of metal oxide particles, as measured by the transmission electron microscope and energy dispersive X-ray analyzer.

10. Metal oxide particles having cores comprising larger molar amounts of zirconia than of ceria, and surface layers comprising larger molar amounts of ceria than of zirconia.

11. The metal oxide particles according to claim 10 carrying a noble metal.

12. A method for preparing metal oxide particles with said metal oxide particles having cores comprising larger molar amounts of zirconia than of ceria and surface layers comprising larger molar amounts of ceria than of zirconia, wherein the method comprises:

preparing a solution comprising zirconia sol and ceria sol;
adjusting the pH of the solution within ± 0.5 on the basis of the isoelectric point of zirconia; and
aggregating zirconia and then aggregating ceria around the aggregated zirconia from said solution to make aggregates.

13. The method according to claim 12 further comprising drying and firing the aggregates.

14. The method according to claim 12 wherein the metal oxide particles have a mean particle diameter of 500 nm or less.

15. The method according to claim 12 wherein the molar ratio of Zr:Ce in the metal oxide particle is 1:0.5 to 0.5:1.

5

10

15

20

25

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35

40

45

50

55

Fig.1

